Electronic Supplementary Information

Structural Complexity Induced by {110} Blocking of Cysteine in Electrochemical Copper Deposition on Silver Nanocubes

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1. Detailed Experimental Procedure

Chemicals. Silver trifluoroacetate (CF_3COOAg, 99.99%, Aldrich), sodium hydrosulfide nonahydrate (NaHS, Aldrich), hydrochloric acid (HCl, 35.0%, Junsei), poly(vinylpyrrolidone) (PVP, Mw = 55 000, Aldrich), ethylene glycol (EG, 99%, J.T. Baker), copper(II) chloride ($CuCl_2$, 99,999%, Aldrich), sodium fluoride (NaF, 99.99%, Aldrich), cysteine (Aldrich) were used as received. Millipore-filtered water (18.3 MΩ cm) was used for the electrolyte solution.

Characterization. The nanostructures were characterized by scanning electron microscopy (SEM, Veiros 460 Fei, KAIST) operated at 10 kV and 100 pA. X-ray diffraction (XRD) patterns were recorded on a Smartlab diffractometer. The diffraction patterns were measured with the samples on the ITO substrate after washing with distilled water. X-ray photoelectron spectroscopy (XPS) was conducted by using a K-alpha spectrometer with an Al Kα X-ray source.

Synthesis of Silver Nanocubes. The colloidal Ag nanocubes are synthesized using a modified polyol process according to the literature.[1] 5.0 mL of EG was prepared in a 100 mL round bottom flask and heated until 150 °C with stirring. Then, 60 μL of 3.0 mM NaHS in EG was injected into the boiling solution. After 2 min of injection, 0.50 mL of 3.0 mM HCl in EG and 1.3 mL of 20 mg mL^{-1} PVP in EG were added. After another 2 min, 0.40 mL of 280 mM CF_3COOAg in EG was added into the mixture, followed by reflux for 90 min and cool down to room temperature. For purification, the mixture was centrifuged with ethanol and dispersed in 30 mL of ethanol.

2. Supplementary Notes

Converting Process of RGB Information to the Maximum Peak Wavelength. The converting process used the color information captured by a dark-field microscope and extracted the maximum scattering peak wavelength.

$$I = VR * 0.299 + VG * 0.5876 + VB * 0.114 \tag{1}$$

$$X = 0.412 * R + 0.358 * G + 0.180 * B \tag{2}$$

$$Y = 0.213 * R + 0.715 * G + 0.072 * B \tag{3}$$

$$Y = 0.019 * R + 0.119 * G + 0.950 * B \tag{4}$$

$$x = X/(X + Y + Z) \tag{5}$$

$$y = Y/(X + Y + Z) \tag{6}$$

A Matlab program was used to convert the RGB information (VR, VG, VB) in the dark-field image into the information about scattering light λ_{max}. The RGB information was extracted from all pixels in an individual particle, then the intensities were calculated according to the equation (1). Among the pixels, the RGB value of the brightest pixel was converted to the x, y values by the equation (2-6). The x, y values were the coordinates of the CIE1931 chromaticity diagram. The outer curved boundary of the diagram represents a monochromatic locus. By drawing a straight line with two points (E and x, y point), we could get another point on the boundary of the diagram, which was the closest monochromatic light. We used the wavelength as the maximum peak of the nanoparticles.[2,3]

3. Supplementary Figures
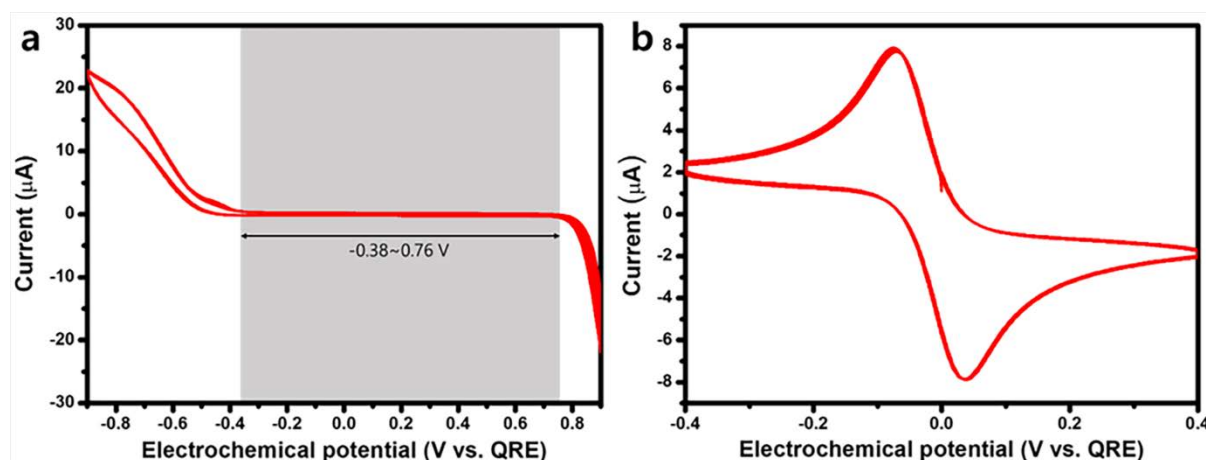
Fig. S1 (a) Cyclic voltammetry (CV) curves to confirm the potential window of ITO glass in the range of -0.9 to 0.9 V. (b) CV for ten consecutive cycles using an electrochemical cell containing 0.1 mM potassium ferrocyanide and 0.1 M NaF in aqueous solution.
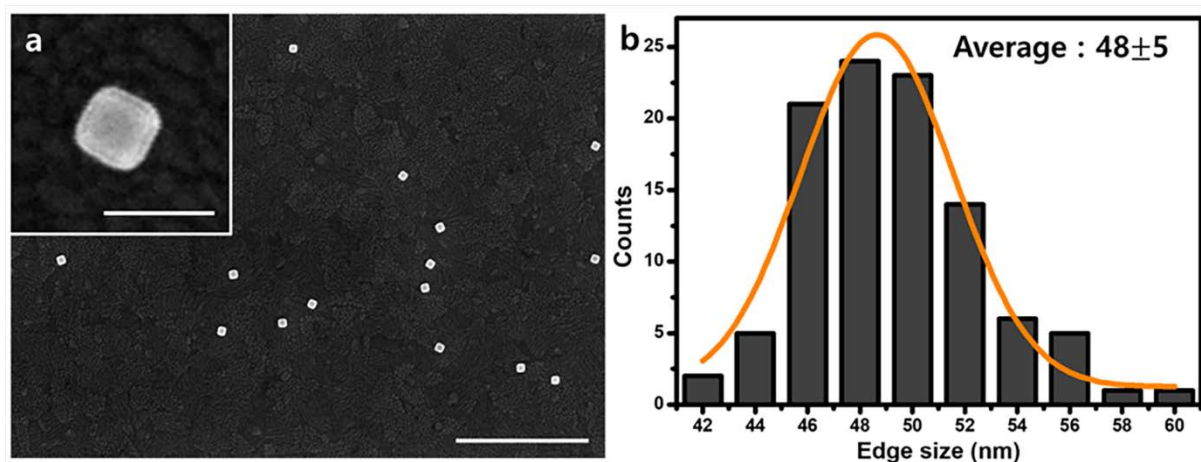

Fig. S2 (a) The SEM image and (b) size-distribution histogram of Ag nanocubes synthesized by the polyol process. The average value and standard deviation were obtained by Gaussian fitting. The scale bars represent (a) 1 μm and (inset) 100 nm.
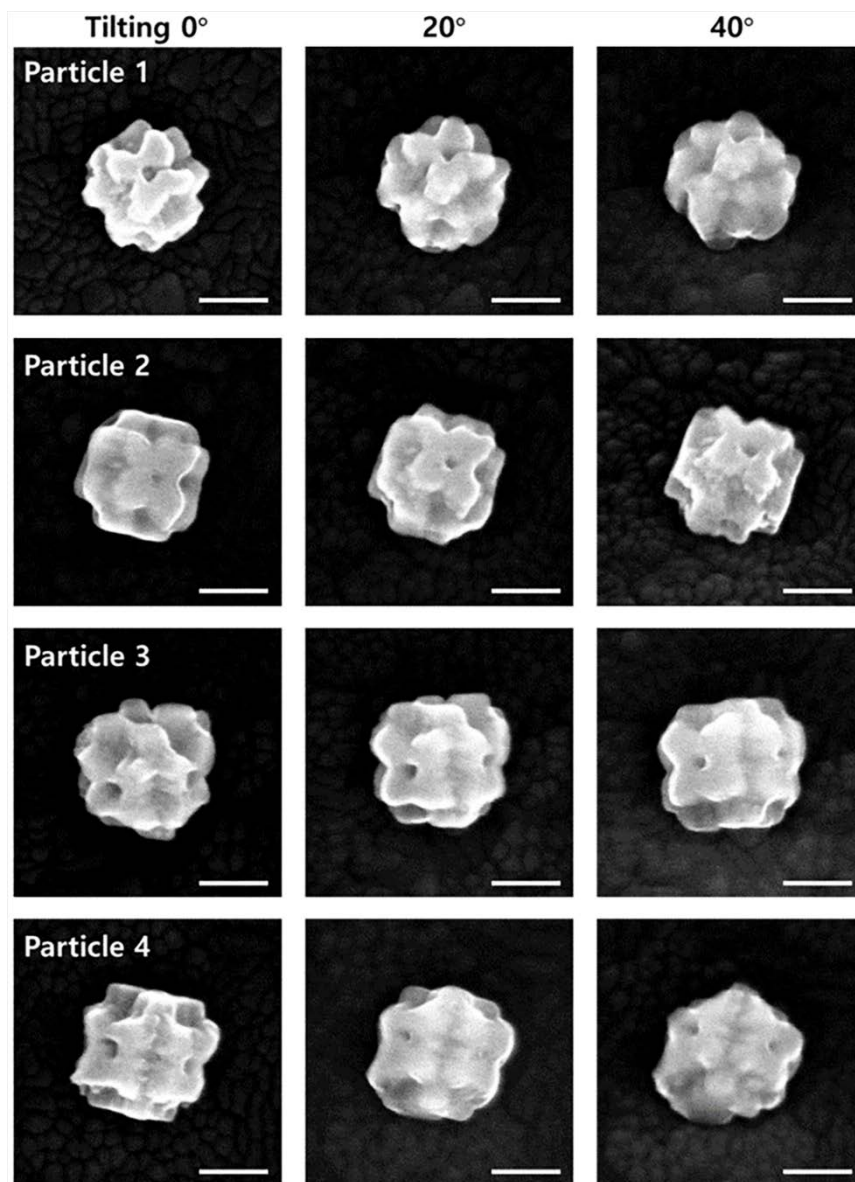
Fig. S3 SEM images tilted by 0°, 20°, and 40°, of four individual windmill nanoparticles. The scale bars represent 100 nm.
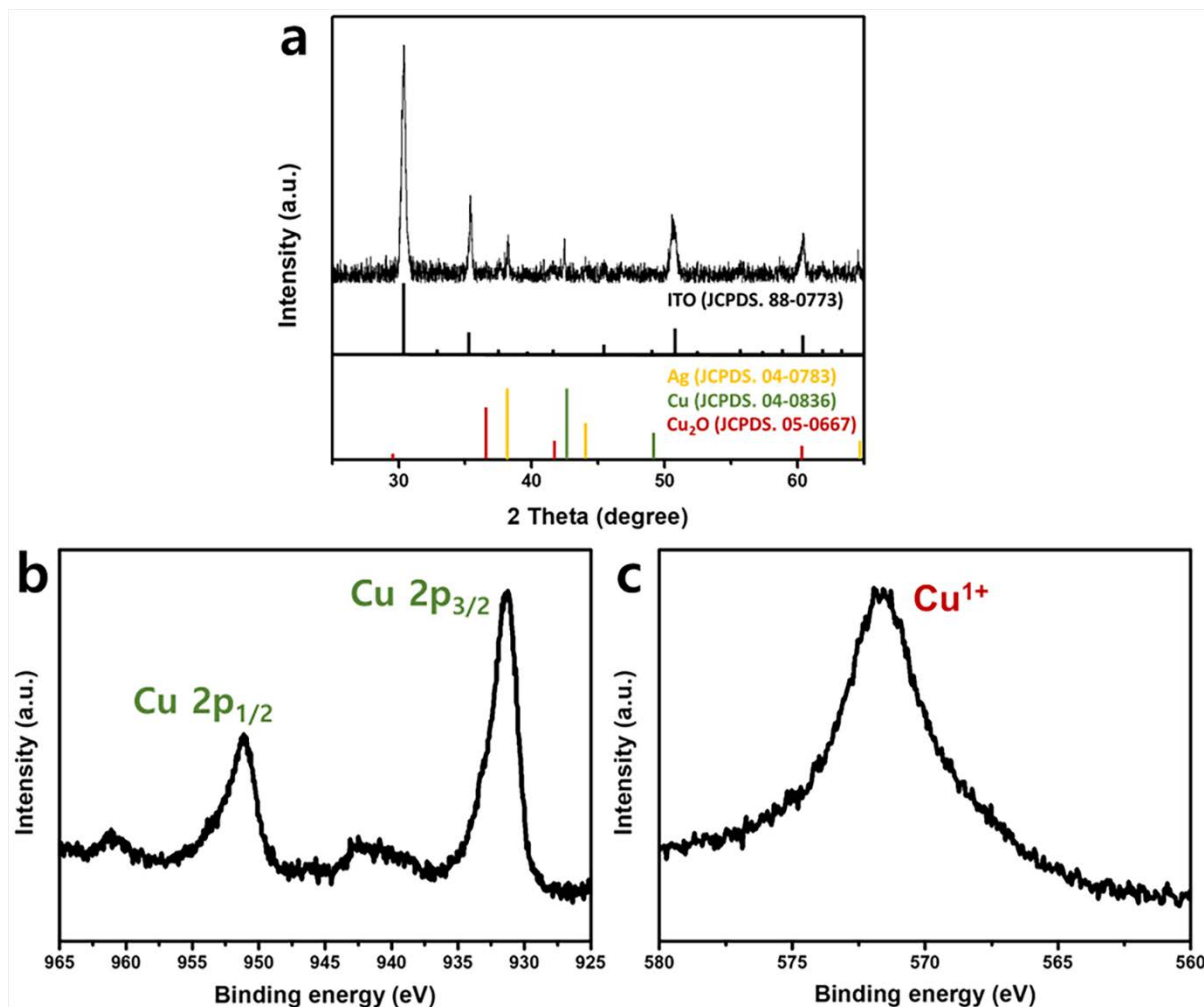
Fig. S4 (a) XRD spectrum, (b) XPS spectrum at the Cu2p region, and (c) Auger spectroscopy at the Cu LMM region of the windmill nanoparticles.
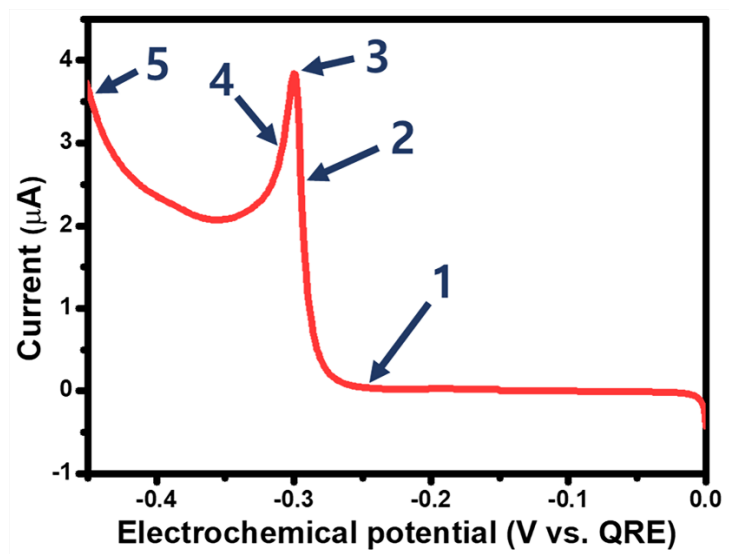
Fig. S5 Linear sweep voltammogram and experimental conditions of potential sweeping for **1** to **5** at the sweep rate of 0.1 mV s^{-1}.
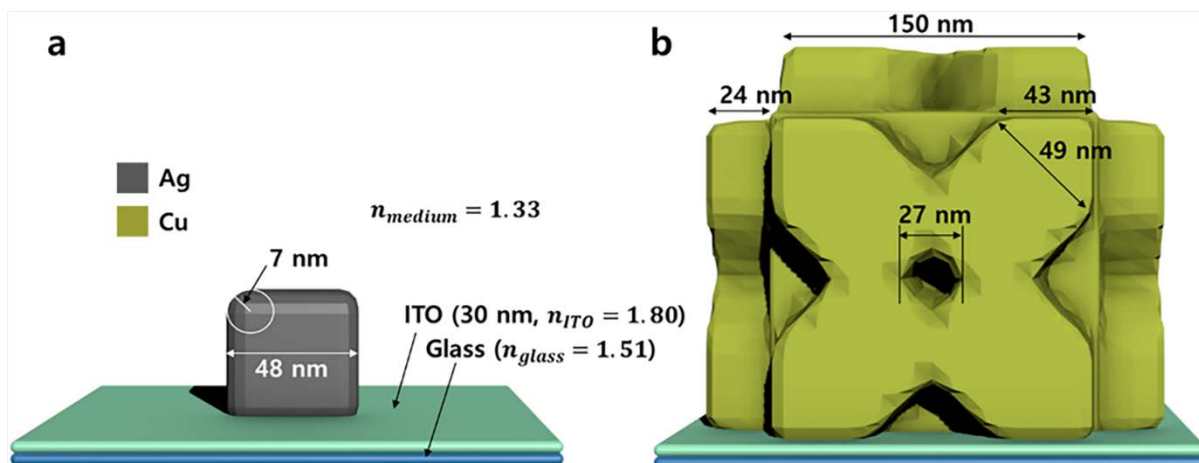
Table S1. The largest Cu thicknesses of **2**, **3**, and **4** along the <100>, <111>, and <110> directions from the original Ag cube surface.
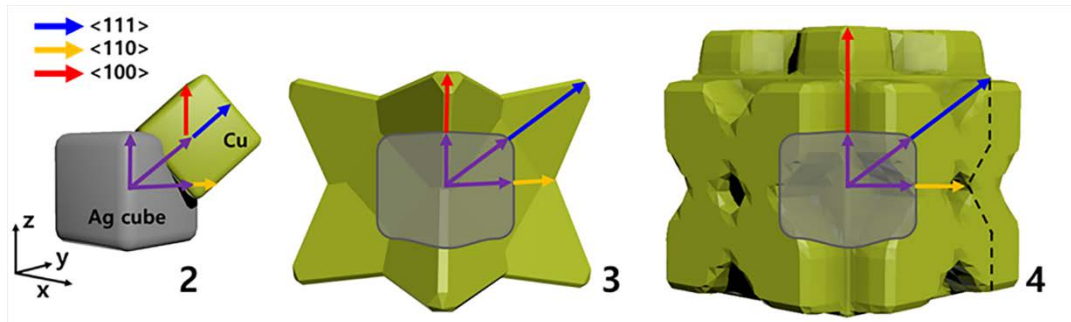
- The largest Cu thickness along the growth direction (nm)

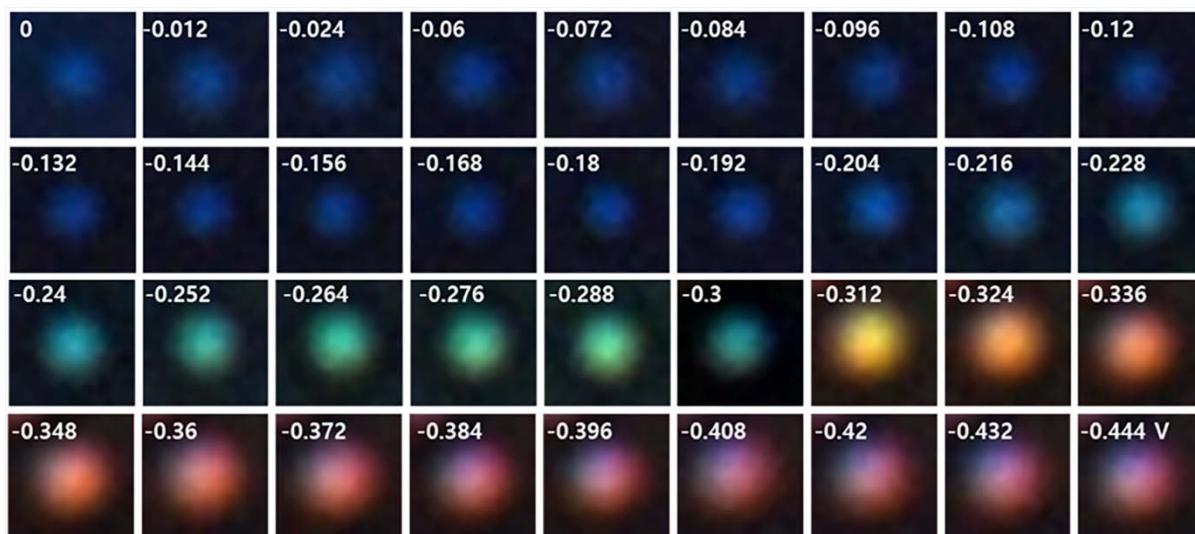| Growth direction / Particle #	<111>	<110>	<100>
2	28	12	33
3	68	22	47
4	77	24	73

Fig. S6 Structural modeling of (a) the original Ag nanocube and (b) the windmill morphology for FDTD calculations.
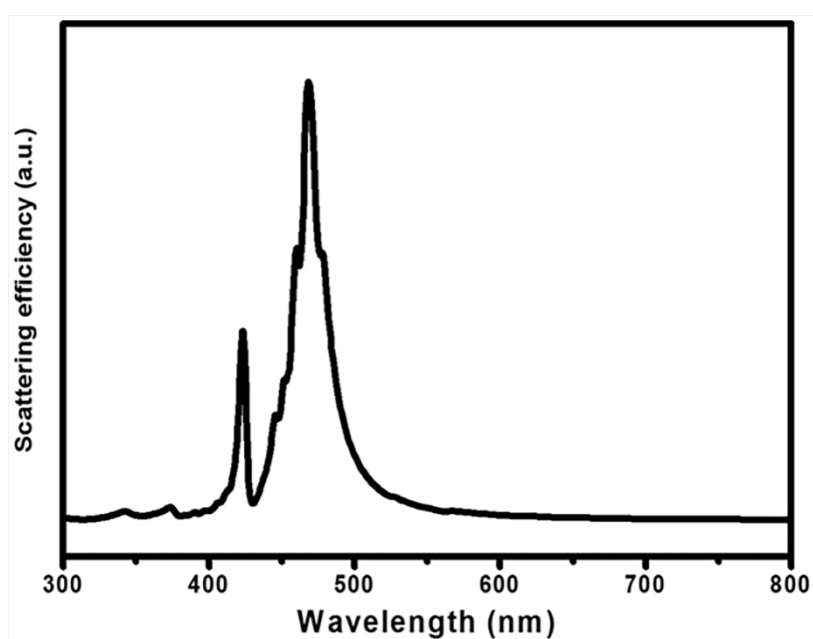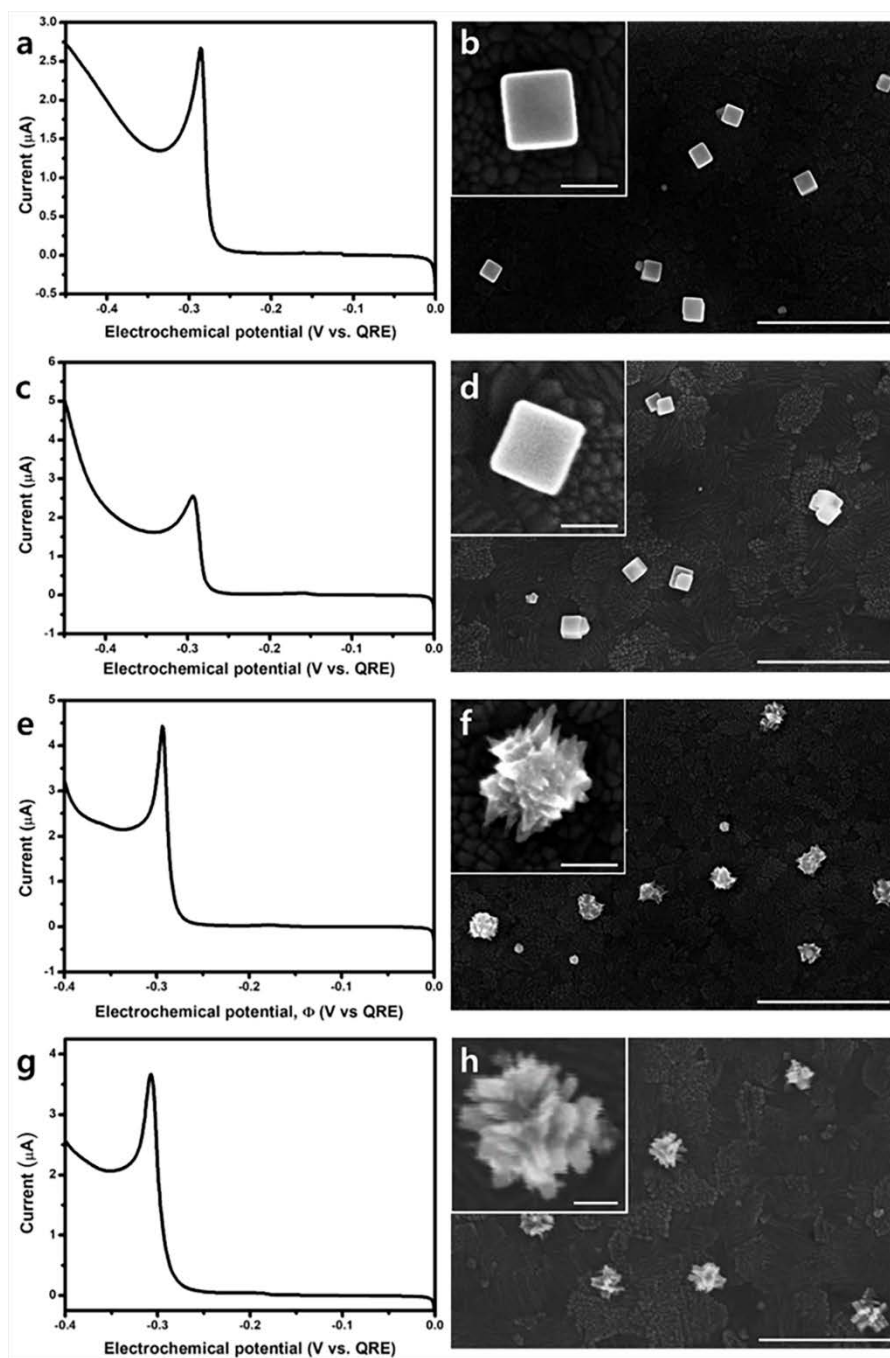

Fig. S7 Theoretical plasmon scattering efficiency of the Ag nanocube by the FDTD simulation.

Fig. S8 Dark-field plasmon scattering images of an individual nanoparticle as a function of applied potential at the sweep rate of 0.1 mV s^{-1}.
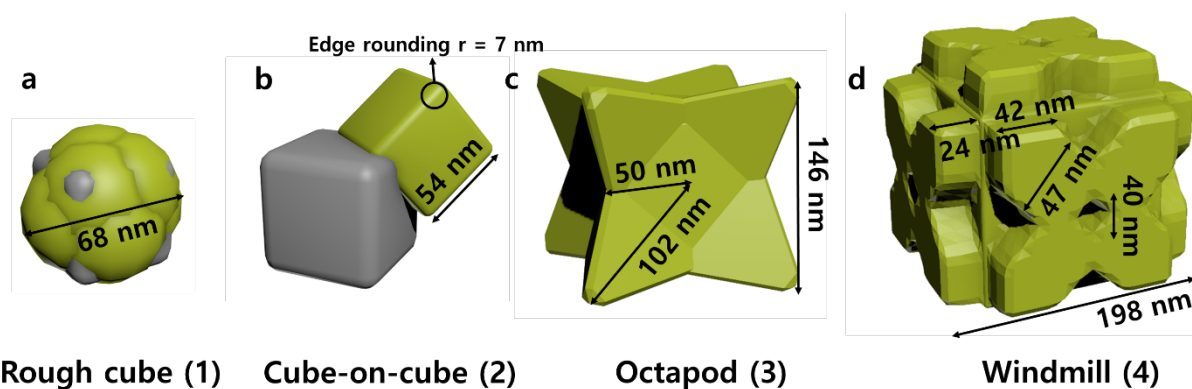
Fig. S9 Structural modeling of (a) rough cube, (b) cube-on-cube, (c) octapod, and (d) windmill morphology for FDTD calculations.

Fig. S10 (a,c,e,g) Linear sweep voltammetry curves and (b,d,f,h) SEM images of the particles after Cu deposition at the sweep rate of 0.1 mV s^{-1} with the cysteine concentration of (a,b) 0, (c,d) 0.1, (e,f) 2.25, and (g,h) 10 μM, respectively. The scale bars represent (b,d,f,h) 1 μm and (inset) 100 nm.
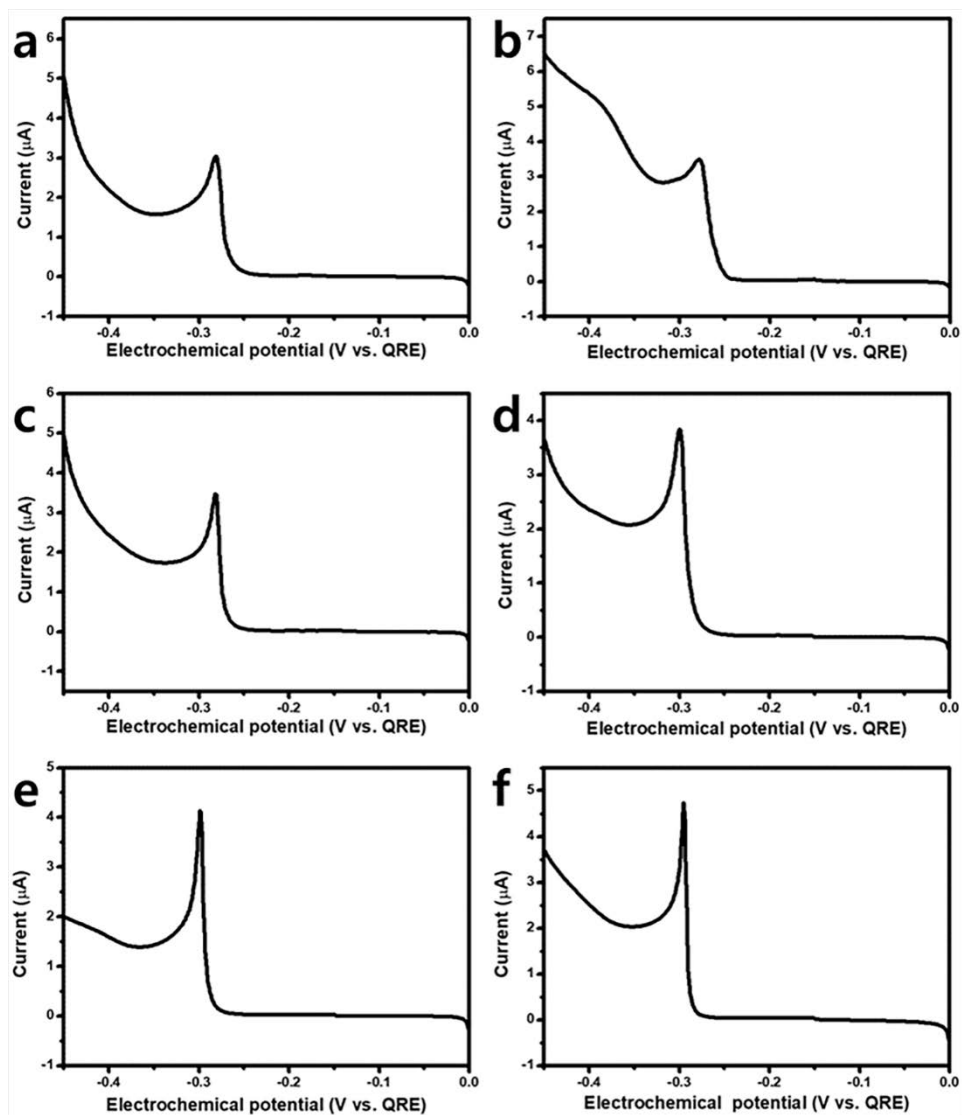
Fig. S11 Linear sweep voltammetry curves at the sweep rate of 0.1 mV s^{-1} with the cysteine concentration of (a) 0.25, (b) 0.5, (c) 0.75, (d) 1, (e) 1.25, and (f) 2 μM, respectively.

4. References

1   Q. Zhang, W. Li, L.-P. Wen, J. Chen and Y. Xia, *Chem. Eur. J.*, 2010, **16**, 10234.

2   Y. Park, H. Oh, J. Park, W. Choi, H. Ryu, D. Seo and H. Song, *J. Phys. Chem. C*, 2019, **123**, 23113.

3   J. Hao, B. Xiong, X. Cheng, Y. He and E. S. Yeung, *Anal. Chem.*, 2014, **86**, 4663.